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We report the experimental results of the valence band offset at a ZnO/GaN (0001) heterointerface. The ZnO/GaN (0001) heterointerface is prepared by growing a ZnO layer on (0001) GaN/Al_2O_3, in which the ZnO layer is epitaxially deposited by plasma-assisted molecular-beam epitaxy, while the GaN template is prepared by metalorganic chemical-vapor deposition. *Ex situ* ultraviolet and x-ray photoelectron spectroscopy have been used to measure the valence band offset ΔE_V. The photoelectron spectroscopy measurements are done before and after Ar^+ ion cleaning of the surfaces. Type-II band alignments with band offsets of $\Delta E_V = 1.0$ eV (before cleaning) and 0.8 eV (after cleaning) with the valence band maximum of GaN being placed above that of ZnO are obtained. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1372339]

Since ZnO has a direct band gap of 3.37 eV at room temperature with a large exciton binding energy of 60 meV and a strong cohesive energy of 1.89 eV, it is regarded as a promising material for exciton-based optoelectronic devices in the ultraviolet region.[1] Most recently, excitonic lasing at room temperature under optical pumped conditions have been demonstrated, which has been followed by the demonstration of high-temperature stimulated emission up to 550 K.[2] By improving the crystallinity of ZnO epilayers, it is possible to realize the formation of excitonic molecules in ZnO,[3] which should lead to extremely large nonlinear optical effects. Although highly conductive *n*-type ZnO can be obtained by proper selection of donor impurities,[4] the growth technique for conductive *p*-type ZnO has not been yet established. In view of such a situation, hetero $p-n$ junctions can be used instead of homo $p-n$ junctions in optoelectronic devices. The GaN/ZnO heterostructure is a promising candidate for such applications, since *p*-type GaN is available and there is only a slight lattice mismatch of 1.9%. The most recent report on the growth of high-quality ZnO epilayers on GaN templates is also encouraging.[3]

Band-line-up data for the ZnO/GaN heterostructure are highly needed in optoelectronic device applications. The valence band of GaN was estimated to be located 0.6 eV above the valence band of ZnO based on the electron affinity rule,[5] while this value is estimated to be 0.24 eV using the valence-band Schottky barrier height.[6] Most recent *ab initio* calculation of electronic structures of ZnO/GaN interfaces predicts that the valence band offset (ΔE_V) varies from 1.0 to 2.2 eV depending on the interface configuration with an average value being 1.6 eV.[7] It is obvious that direct measurements of the band offset at the ZnO/GaN heterojunction with well-defined interface are highly required. This letter reports the ΔE_V at a (0001) ZnO/GaN heterointerface measured by ultraviolet (UPS) and x-ray photoelectron spectroscopy (XPS).

ZnO films were grown on (0001) GaN/Al_2O_3 by plasma-assisted molecular-beam epitaxy (MBE), in which 4-μm-thick GaN films had been predeposited on (0001) Al_2O_3 by metalorganic chemical-vapor deposition (MOCVD). The GaN has Ga polarity with a Ga-terminating surface on top and is *n*-type with typical carrier concentration of $8.18 \times 10^{18}\,cm^{-3}$ and mobility of 197 $cm^2/V\,s$. After degreasing, a GaN template was thermally cleaned in the MBE chamber at 700 °C for 30 min. Prior to ZnO growth, GaN surface was exposed to Zn beam for 1 min to prevent the oxidation of the

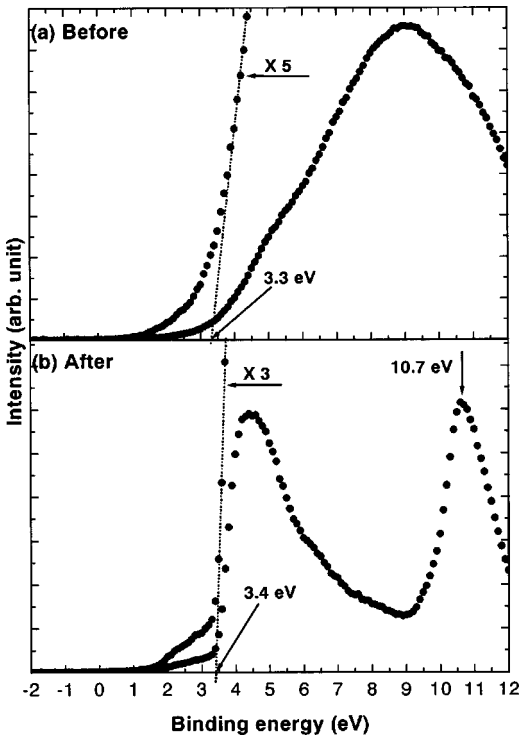

FIG. 1. UPS valence band spectra obtained from the 65-nm-thick ZnO film grown on a GaN film predeposited on Al_2O_3. Before (a) and after (b) Ar^+ ion cleaning. The peak at around 10.7 eV in (b) corresponds to the Zn 3*d* state.

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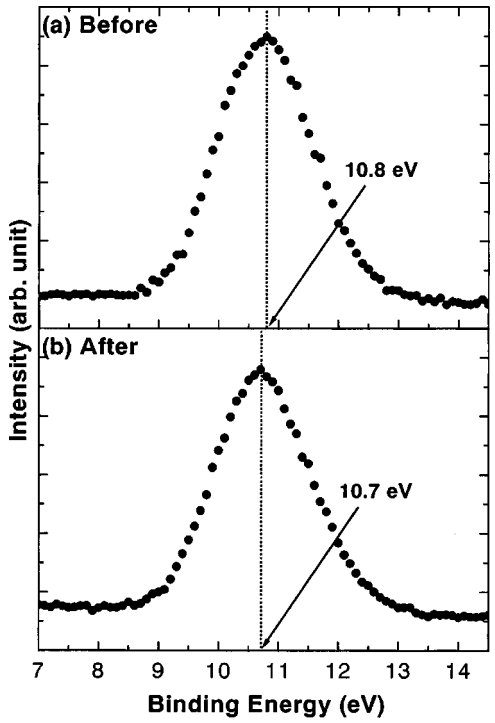

FIG. 2. XPS Zn 3*d* core level spectra obtained from the 65-nm-thick ZnO film grown on a GaN film predeposited on Al_2O_3. Before (a) and after (b) Ar^+ ion cleaning.

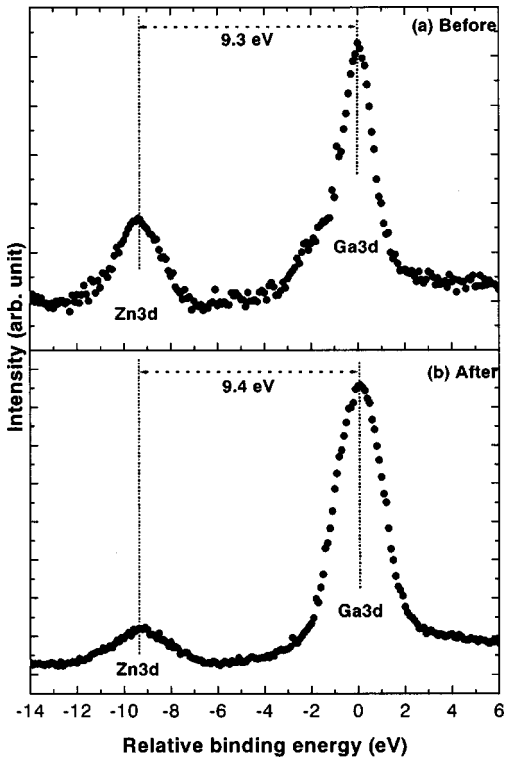

FIG. 3. XPS spectra of Ga 3*d* and Zn 3*d* core level peaks obtained from upper ZnO and lower GaN films with a ZnO/GaN heterointerface. Before (a) and after (b) Ar^+ ion cleaning. (The energy scale is relative to the Ga 3*d* level.)

GaN surface, which would otherwise result in Ga-oxide interface layers at the ZnO/GaN interface.[8] As a result of Zn preexposure, no interface layer was formed. The interface bonding sequence was confirmed to be ...N–Ga–N–Ga–O–Zn–O–Zn... through extensive investigation by transmission electron microscopy and coaxial impact collision ion scattering spectroscopy.[9] Details of the ZnO/GaN interface structure has been reported elsewhere.[10] As grown undoped ZnO films would show *n*-type conductivity, as usual.[11] Three sets of samples were prepared for XPS and UPS studies: (1) a GaN template to measure the valence band maximum (VBM) and the Ga 3*d* core level (CL) of GaN, (2) a 65-nm-thick ZnO film grown on GaN template to measure VBM and Zn 3*d* CL of ZnO, (3) a 2-nm-thick ZnO film grown on GaN template to measure the difference in CLs of Ga 3*d* and Zn 3*d* at the ZnO/GaN heterointerface.

All the UPS and XPS experiments were performed using an ultrahigh vacuum XPS/UPS combined system. UPS measurements were performed using the 21.22 eV He I line with an energy resolution of 61.5 meV, while the dual x-ray lines of Al $K\alpha$ (1486.5 eV) or Mg $K\alpha$ (1253.6 eV) was used for XPS measurements. The binding energies were corrected by referring the Au $4f_{7/2}$ energy for XPS and Au Fermi level (FL) for UPS. UPS and XPS measurements were performed at 40.2 K both on as-prepared samples and on cleaned surfaces by Ar^+ sputtering at ion beam voltage of 1.0–1.5 kV and current of 30–40 μA for 10–120 s. Cleanliness of the GaN surface by Ar^+ sputtering was checked by monitoring decrease in the intensities of C 1*s* and O 1*s* XPS peaks to noise level and disappear of N–O bonds at 410.0 eV from the N 1*s* XPS peak. In the case of ZnO, decrease in the intensity of the C 1*s* XPS peak to noise level and disappear of shoulder at 534 eV, which can be assigned to H_2O bonds, from the O 1*s* XPS peak were monitored to confirm the cleanliness. The method used for measuring the ZnO/GaN valence band discontinuity was similar to that of Waldrop and Grant,[12] can be described by the following formula:

$$\Delta E_V(\mathrm{ZnO/GaN}) = (3d-\mathrm{VBM})^{\mathrm{GaN}}_{\mathrm{bulk}} - (3d-\mathrm{VBM})^{\mathrm{ZnO}}_{\mathrm{bulk}} - (3d^{\mathrm{GaN}} - 3d^{\mathrm{ZnO}})_{\mathrm{interface}}.$$

First we discuss the VBM of GaN, which was determined from UPS spectrum. We noticed that the dominant features in the valence band UPS spectra of our GaN film were similar as those previously reported.[13] We determined the VBM of GaN before cleaning as 3.2 eV, which lies in the range of the reported value from 2.7 to 3.5 eV,[13,14] relative to the FL. After cleaning, the VBM of GaN decreased to 1.9 eV. A similar shift in the VBM of GaN varying from 3.5 to 2.0 eV by Ar^+ cleaning was previously reported.[13] Since the band gap energy of GaN is 3.4 eV, FL before Ar^+ bombardment should be located close to the conduction band minimum (CBM) at the surface and this implies a flat band at the surface of the *n*-GaN. As the VBM relative to FL shifts from 3.2 to 1.9 eV by Ar^+ cleaning, FL at surface shifts from the vicinity of CBM into the band gap. Such a shift of FL into the band gap of GaN can be caused by surface states due to excess metallic Ga clusters on the surface formed by Ar^+ bombardment, which would induce N deficiency.[13]

Next, we discuss the binding energy of Ga 3*d* CL of GaN measured by XPS. The Ga 3*d* peak is observed at 21.0 eV before cleaning and shifted to 19.4 eV after cleaning. A similar low energy shift, which is consistent with the VBM shift, in the Ga 3*d* peak from 20.7 to 19.4 eV by cleaning was also reported previously.[13] The differences between

TABLE I. Summaries of binding energies obtained from thick GaN, ZnO films and ZnO/GaN heterointerface before and after Ar^+ ion cleaning (in electron volts).

	GaN^{VBM} (thick GaN)	Ga 3*d* (thick GaN)	Ga 3*d*−GaN^{VBM}	ZnO^{VBM} (thick ZnO)	Zn 3*d* (thick ZnO)	Zn 3*d*−ZnO^{VBM}	Ga 3*d*−Zn 3*d* (ZnO/GaN interface)	Valence band offset ΔE_v
Before	3.2	21.0	17.8	3.3	10.8	7.5	9.3	1.0
After	1.9	19.4	17.5	3.4	10.7	7.3	9.4	0.8

VBM and Ga 3*d* CL energies were 17.8 and 17.5 eV before and after cleaning, respectively. These values lie within the range of previously reported ones, in the range of 17.1–18.4 eV (see Ref. 14, and references therein). The Ga 3*d* peak is broadened by 0.9 eV with its full width at half maximum (FWHM) value varying from 1.6 to 2.5 eV after cleaning. The band bending of the *n*-GaN after Ar^+ cleaning is estimated to be about 1.5 eV from the difference between CBM and FL at surface. The depletion layer thickness is calculated to be 14 nm from the carrier (*n* type) concentration $8.18 \times 10^{18}\,cm^{-3}$ and relative dielectric constant 9.5 of GaN. From the electrostatic potential profile, the band bending in the range of escape depth (2.5 nm) of photoelectron induces about 1 eV of FWHM broadening of the CL peak. The broadening of Ga 3*d* peak after Ar^+ ion cleaning could be explained also as a result of nitrogen deficiency by Ar^+ cleaning.

Now, we discuss XPS and UPS results from a 65-nm-thick ZnO film. Figures 1(a) and 1(b) show UPS spectra before and after cleaning. The feature peaks and their positions in the UPS spectrum after cleaning agree very well with previously reported UPS results on (0001) ZnO.[15] Based on the previous UPS study on ZnO, the observed features at 4.5, 6.1, and 7.5 eV in Fig. 1(b) can be attributed to ''Zn 4*p*–O 2*p* derived (or Zn 3*d*–O 2*p* interaction),'' ''indirect transition process,'' and ''Zn 4*s*–O 2*p* mixed bulk state,'' respectively.[15,16] The top of the ZnO valence band is mainly contributed by ''Zn 4*s*–O 2*p* derived'' states.[16] From Figs. 1(a) and 1(b), we determined the VBM energies of ZnO as 3.3 and 3.4 eV before and after cleaning, respectively. The VBM value for cleaned ZnO surface agrees well with a previous report of 3.6 eV.[15] Figures 2(a) and 2(b) show Zn 3*d* XPS spectra before and after cleaning. The peak position of Zn 3*d* shifts from 10.8 to 10.7 eV by Ar^+ cleaning. Those values agree well with previously reported Zn 3*d* peak positions at around 10.5 eV.[15,17] In contrast to GaN, the shift of VBM and the core level by cleaning is not significant in the case of ZnO. This difference is tentatively ascribed to less surface contamination and/or change in surface stoichiometry by cleaning on the ZnO surface. Based on Figs. 1 and 2, we determined the difference between VBM and Zn 3*d* level as 7.5 and 7.3 eV, respectively, before and after cleaning.

Figures 3(a) and 3(b) show XPS spectra for Ga 3*d* and Zn 3*d* CLs of a ZnO/GaN heterostructure sample before and after cleaning, respectively. The differences between the CL energies of Ga 3*d* and Zn 3*d* are determined as 9.3 and 9.4 eV before and after cleaning. We have determined the valence band alignment at the ZnO/GaN heterointerface as type-II band alignments with $\Delta E_V = 1.0\,eV$ (before Ar^+ cleaning) and 0.8 eV (after Ar^+ cleaning) with the VBM of GaN being located above that of ZnO. Table I summarizes the experimental results obtained in the present study. Here, it should be noted that the values of (Ga 3*d* − VBM) for GaN was changed only by 0.3 eV through Ar^+ cleaning, which should be compared with the changes of the VBM (1.3 eV) and Ga 3*d* (1.6 eV) energies by Ar^+ cleaning. This indicates that VBM and Ga 3*d* levels shift similarly following the shift of FL at surface. In the case of ZnO, both VBM and Zn 3*d* energies showed only slight change by Ar^+ cleaning. Such a tendency results in reliable estimation of ΔE_V values irrespective of surface condition.

In summary, we have determined the band alignment at a (0001) ZnO/GaN heterointerface by *ex situ* UPS and XPS measurements. All the results are compared before and after Ar^+ cleaning of the surfaces. The type-II band alignment at the ZnO/GaN heterointerface is concluded with the VBM of GaN being located above that of ZnO. The ΔE_V at the ZnO/GaN heterointerface is, respectively, estimated to be 1.0 and 0.8 eV before and after cleaning.

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